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13. ABSTRACT (Maximum 200 words)

The effect of large magnitude electric fields on polymer thin films is investigated in order to improve poling efficiencies in polymer films for second order nonlinear optical applications. This research determines the charge distribution, symmetry, and magnitude across doped and undoped glassy polymer thin films as a function of temperature, time, and poling (processing). Electrochromism, second order nonlinear optics, dielectric relaxation, isothermal current and surface voltage decay measurements will be used to determine the material properties. Trapping levels and sites will also be examined. By using dielectric relaxation and optical techniques we will explore how applied electric fields affect rotational mobility of small chromophores in polymer hosts. We expect to be able to improve poling efficiency and thus device performance both by achieving the greatest possible fields with the best magnitude and symmetry characteristics, and enhancing the temporal and thermal properties of the films by manipulating their charge storage and transport properties. This understanding will allow the most efficient development and design for nonlinear optical materials.

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1. Lackritz, H.S.; Torkelson, J. M. "Polymer Physics of Poled Polymers for Second Order Nonlinear Optics" Chapter 8 in *Molecular Optoelectronics: Materials, Physics, and Devices*, Zyss, J., Ed. Academic Press, New York, **1993**, 337.

2. Haber, K. S.; Ostrowski, M. H.; *Lackritz, H. S. "Characterizing the Distribution of Space Charge in Poled Polymer Films" *Materials Research Society Symposium Series*, **1994,***328*, xxx.

3. Pasmore, T.; Talbot, J.; Lackritz, H. S. "Monte-Carlo Simulations of Electric Field Hopping in Doped Polymer Thin Films" *Nonlinear Optics*, in review.

4. Lackritz, H. S.; Ostrowski, M. H.; Liu, L.-Y.; Fu, C.Y. S.; "Dielectric Relaxation and Electric Field Effects in Polymers For Second Order Nonlinear Applications" *Polym. Mater. Sci. Eng. Preprints*, **1994**, *70*, 392.

Other publications this year:

1. Fu, C.-Y. S.; Lackritz, H. S.; Priddy, D. B.; McGrath, J. E. "Synthesis and Characterization of High Temperature Stable Polymers for Second Order Nonlinear Optical Applications" *Materials Research Society Symposium Series*, **1994,***328*, 589.

2. Priddy, D. B.; Fu, C.-Y. S.; Lackritz, H. S.; *McGrath, J. E. "Phosphorus Containing Poly(arylene ether)s as Second Order Nonlinear Optical Materials" *Materials Research Society Symposium Series*, **1994,***328*, 547.

3. Wright, M. E.; Mullick, S.; Lackritz, H. S.; Liu, L.-Y. "Organic NLO Polymers. 2. A Study of Main Chain and Guest-Host $\chi^{(2)}$ NLO Polymers: NLO-phore Structure Versus Poling" *Macromolecules*, **1994**, May, XXX.

4. Wright, M.E.; Toplikar, E.G.; Lackritz, H.S.; Kerney, J.T. "Organometallic NLO Polymers 4. Organometallic Main-Chain, Side-Chain, and Guest-Host Polymers: A Study of Their Orientation and Relaxation Using Second Harmonic Generation" *Macromolecules*, **1994**, May, XXX.

5. Wright, M. E.; Toplikar, E. G.; Lackritz, H. S.; Kerney, J. T. "New Organometallic Polymeric Materials: The Search for Organometallic NLO Polymers" in *Inorganic and Organometallic Polymers*, Alcock, H., Wynne, K., and Wisian-Neilson, P., Eds., ACS Symposium Series #XXX, American Chemical Society, Washington, D.C. **1994**, in press.

6. Hampsch, H. L.; Yang, J.; Wong, G. K.; Torkelson, J. M. "Dopant Orientation Dynamics in Doped Second Order Nonlinear Optical Amorphous Polymers. 3. Effect of Hydrogen Bonding" *J. Polym. Sci., Polym. Phys.*, in press.

7. Mitchell, M. A.; Tomida, M.; Hall, H. K. Jr.; Lackritz, H. S.; Robello, D. R.; Willand, C. S.; Williams, D. J. "Synthesis and Investigation of the Nonlinear Optical Properties of Various p-Aminophenyl Sulfone Oligomers" *Chem. Mat.*, in press.

8. Wright, M.E.; McFarland, E.; Petteys, B. J.; Lackritz, H.S.; Liu, L.-Y. "Organic NLO Polymers. 3. Homopolymerization of Indole Based NLO-phores. A Heterocycle $\chi^{(2)}$ NLO Main-Chain Polymer" *Macromolecules*, in review.

9. Liu, L. Y.; Ramkrishna, D.; Lackritz, H. S. "The Rotational Brownian Motion of Chromophores and Electric Field Effects in Polymer Films for Second

Order Nonlinear Optics I: Theory and Experiment" *Macromolecules,* submitted 2/94.

10. Liu, L. Y.; Lackritz, H. S. "The Rotational Brownian Motion of Chromophores and Electric Field Effects in Polymer Films for Second Order Nonlinear Optics II. Applications" *Macromolecules,* submitted 2/94.

11. Lackritz, H. S.; Willand, C. S.; Robello, D. R.; Williams, D. J. "Electric Field Effects in Second Order Nonlinear Optical Polymers" *J. Appl. Phys.,* to be submitted; awaiting Kodak approval.

12. Lackritz, H. S., Book Review on "Polymers for Lightwave and Integrated Optics: Technology and Applications," Ed. L. A. Hornak *AIChE J.,* **1993,** *39,* 1738.

13. Wright, M. E.; McFarland, I.; Pettys, B. J.; Lackritz, H. S.; Liu, L. Y. "Organic NLO Polymers. 5. Homopolymerization of Indole Based NLO-phore: A Heterocycle $\chi^{(2)}$ Main-Chain Polymer" *Polymer Preprints* **1994,***35,* 470.

Invited Presentations:

1. *Lackritz, H. S. "Applications of Second Order Nonlinear Optics to the Study of Electric Fields Effects and Polymer Dynamics" presented at the Department of Chemical Engineering, University of Cincinnati in Cincinnati, OH, January 1993.

2. *Lackritz, H. S.; Liu, L. Y.; Hawley, J. C. "Applications of Second Order Nonlinear Optics to the Study of Electric Fields Effects and Polymer Dynamics" presented at the Materials Research Society meeting in San Francisco, CA, March 1993.

3. *Lackritz, H. S. "Polymer Physics and Second Order Nonlinear Optics" presented at the Society of Rheology national meeting, Boston, MA, October 1993.

4. *Lackritz, H. S. "Nonlinear Optical Studies of Poled Amorphous Polymers-Investigations of Polymer Relaxations and Chromophore Rotational Diffusion" presented at Pennsylvania State University in University Park, PA, November 1993.

5. *Lackritz, H. S. "Polymer Physics Studied Using Second Order Nonlinear Optics" presented at the Dow Chemical Company Corporate Research Laboratories in Midland, MI, December 1993.

6. Ostrowski, M.; Haber, K.; *Lackritz, H. S. "Electric Field Effects in Polymers for Second Order Nonlinear Optics" presented at the International Conference on Organic Nonlinear Optics in Val Thorens, France, January 1994.

7. *Lackritz, H. S; Hughes, J. C.; Subramanyan, S. "Polymers for Second Order Nonlinear Optics and Optical Holography" presented at Hoechst-Celanese Corporation in Charlotte, NC, January, 1994.

8. Liu, L. Y.; *Lackritz, H. S. "Dielectric Relaxation in Second Order Nonlinear Optical Polymer Systems" presented at the American Chemical Society meeting in San Diego, CA, March 1994.

9. *Lackritz, H. S. "Polymers for Second Order Nonlinear Optics" presented at the Golden Gate Polymer Forum in San Francisco, CA, March 1994.

10. *Lackritz, H. S. "Photorefractive Polymers for Second Order Nonlinear Optics" presented at the Field and Optics Seminar, Purdue University, West Lafayette, IN, April 1994.

11. *Lackritz, H. S. "Polymer Physics Studied Using Second Order Nonlinear Optics" presented at the University of Michigan, Department of Materials Science, Ann Arbor, MI, April 1994.

12. *Lackritz, H. S. "Polymer Relaxations in Doped and Functionalized Systems Studied Using Second Order Nonlinear Optics" to be presented at the Society for Photo-optic Instrumentation Engineers meeting in San Diego, CA, July 1994.

13. *Lackritz, H. S.; Liu, L.-Y. "Polymer Relaxations in Doped and Functionalized Systems Studied Using Second Order Nonlinear Optics" to be presented at the American Chemical Society/Optical Society of American meeting in Washington, DC, August 1994.

Contributed Presentations relating to this grant:

1. *Lackritz, H. S. "Polymer Physics and Electric Field Effects in Poled Polymers for Second Order Nonlinear Optics" presented at the Second International Discussion Meeting on Relaxations in Complex Systems in Alicante, Spain, June 1993.

2. *Pasmore, T.; Talbot, J.; Lackritz, H. S. "Monte-Carlo Simulations of Charge Transport in Polymers for Second Order Nonlinear Optics" presented at the Optical Society of America/American Chemical Society national meeting in Toronto, Canada, October 1993.

3. *Ostrowski, M. H.; Haber, K. S.; Lackritz, H. S. "Electric Field Measurements in Molecularly Doped Polymer Thin Film Systems" presented at the Optical Society of America/American Chemical Society national meeting in Toronto, Canada, October 1993.

4. *Haber, K. S.; Ostrowski, M. H.; Lackritz, H. S. "Characterizing the Distribution of Space Charge in Poled Polymer Films" presented at the Materials Research Society meeting in Boston, MA, November 1993.

Sessions Chaired at National Research Meetings:

Session Chair - "Optical Probes and Properties of Polymers," American Physical Society Meeting, March 1993, Seattle, WA.
Session Chair - "Dielectric Relaxation in Polymeric Systems," American Chemical Society Meeting, March 1994, San Diego, CA.
Session Chair and Organizer- "Polymers for Optoelectronics and Photonics," American Institute of Chemical Engineers Meeting, to be held November 1994, San Francisco, CA.

Awards and Honors

Presidential Faculty Fellows Award (National Science Foundation) 1993-1998
Murphy Award for Outstanding Undergraduate Teaching in Chemical Engineering
        1994
Shreve Award for Outstanding Teaching, Second Place, Chemical Engineering,
        1994
Sigma Xi, Scientific Research Society 1994-
Office of Naval Research Young Investigator Award 1992-1995

Electric Field Effects in Polymer Thin Films for Second Order Nonlinear Optical Applications

Hilary S. Lackritz

I. Introduction

Electric field effects on polymer physical properties are important in many areas including photonics, electrophotography and telecommunications.[1,2] Polymers in these areas are widely used as electronic insulators, coatings and cables. Previous work concerning electric field effects on polymers has been done, but only under the conditions of electric field induced breakdown or on bulk polymer samples.[3,4] No work has been done concerning polymer films whose thickness is less than 10μm. The goal of this research is to determine the charge magnitude, symmetry and distribution across polymer thin film systems for second order nonlinear optical applications as a function of time, temperature, thickness, poling and concentration of dopant. In addition, the electric field effects on the orientation of chromophores in the polymer film will also be studied. The primary techniques that will be used are electrochromism, second order nonlinear optics, dielectric relaxation, thermal pulse measurement and total internal reflection fluorescence spectroscopy.

Polymer thin film systems have been explored as potential materials for second order nonlinear optical device applications such as second harmonic generation and linear electro-optic effect.[1] The photonic devices that may use polymer thin film systems as an active media are waveguides and frequency doublers. To obtain a noncentrosymmetric orientation of the chromophores necessary for second order nonlinear effects, the polymer system is poled with a high electric field.[5] The electric field effects due to poling are poorly understood. Therefore, to make efficient nonlinear optical devices, it is necessary to understand the electric field effects on the thermal and temporal stability of chromophore orientation and of the effects of space charges present within the polymer thin film system.

This research presents a novel approach using electrical and optical methods to characterize the electric field effects in polymer thin films. The goals of this research can be summarized as follows:

1) Determine the charge magnitude, symmetry and distribution across polymer thin film as a function of time, temperature, thickness, poling and concentration of dopant using electrochromism, second order nonlinear optics, thermal pulse measurements, and total internal reflection fluorescence spectroscopy.

2) Determine how the applied electric field affects rotational mobility of chromophores in polymer systems using dielectric relaxation, and second order nonlinear optics.

The techniques that will be used are as follows:

1) Electrochromism: To determine charge symmetry and magnitude across polymer thin films.

2) Second order nonlinear optics: To determine charge magnitude across polymer films and to study rotational mobility of chromophores in polymer systems.

3) Dielectric relaxation: To determine the rotational mobility of chromophores in polymer systems.

4) Total internal reflection fluorescence spectroscopy: To determine the charge distribution as a function of thickness.

5) Thermal pulse measurements: To determine charge distribution in polymer systems.

6) Spectroellipsometry: To determine the electrooptic coefficient from the change of index of refraction as a function of an applied static field.

7) Cyclic Voltammetry: To determine the voltage dependence of the capacitance of the film due to trapped charges.

8) Mach Zehnder Interferometry: To determine directly the electrooptic coefficient of the dye-doped polymer thin film.

This research represents an attempt to completely characterize pivotal electric field effects in second order nonlinear optical polymer films so that practical processing methods can be developed for device manufacture and implementation.

II. Research Goals
II.a Determine the charge magnitude, symmetry and distribution across polymer thin film as a function of time, temperature, thickness, poling and concentration of dopant.

Methods Used
The major methods utilized are electrochromism, second order nonlinear optics, thermal pulse measurements, and total internal reflection spectroscopy. Cyclic voltammetry will be used to determine any voltage-dependent capacitance.

II.a.1 Electrochromism:
Key information: *The magnitude of the electric field at the electrodes and of the average electric field across the polymer film is obtained.*
Goals answered: *Charge symmetry at the surfaces and charge magnitude through the polymer film is obtained as a function of poling and concentration of chromophore.*

Construction:
The light source used in this experiment is a 500 Watt Oriel ultraviolet and visible Hg(Xe) lamp, model 66028. A Jobin Yvon monochromator is used to separate the light so one wavelength can be used. A Stanford Research Systems, model DS345, function generator with an University Sound stereo amplifier is used to generate an 1 KHz ac electric field across the sample. A Stanford Research Systems, model SR530, lock-in amplifier is used to collect data. The experiment is computer controlled using LabView software and a Macintosh Quadra 950.

Work to date:
The samples used in these experiments were poly methylmethacrylate (PMMA) films doped with 4-dimethylamino-4'-nitrostilbene (DANS) or p-diethylaminobenz-aldehyde diphenylhydrazone (DEH) (Figure 1). The films were spun using a spin coater onto conductive indium tin oxide coated slides. They were allowed to air dry for 24 hours and then were placed under vacuum in an oven for 24 hours. Next, the temperature was slowly raised above the glass transition temperature and was kept at this temperature for 24 hours. The films were then allowed to cool slowly to room temperature. This process insured that the thermal history and any preferred orientation resulting from spinning were erased. Lastly, a thin layer of gold was evaporated onto the top of the film.

Electroreflection measurements were made within the absorption spectrum of the chromophores which was measured using a Spectronic Genesys 5 ultraviolet-visible (UV-Vis) spectrophotometer. The indium tin oxide coating and the gold on top of the film served as electrodes. A 0.1 - 1 kHz AC voltage was applied across the film to create electric fields approaching 10^6 V/cm. A collimated beam from a Hg-Xe 500W lamp was passed through a monochromator and reflected from the sample. A photodiode connected to a lock-in amplifier

was used to observe the reflected beam. The lock-in amplifier was phased locked to the frequency of the applied field. Another photodiode was used to measure the change in intensity, if any, of the light from the lamp. The output of both photodiodes were recorded as a function of optical wavelength. A spectrum of the sample without the applied electric field was also obtained. The electroreflection setup is shown in Figure 2.
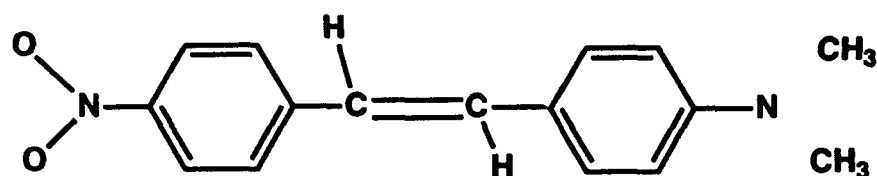
The first derivative of the zero-field reflection spectrum for a 5 wt% DANS doped in PMMA film is shown in Figure 3. In Figure 4, the fundamental and second harmonic spectra for a 5 wt% DANS doped in PMMA film are shown. The same plots for 5 wt% DEH are shown in Figures 5 and 6. The spectral dependence shows no obvious relation to the derivative of the zero-field spectrum. Samples tested for electroreflection signal well to the red of their absoption bands showed minimal signal arguing against a contribution to the signal from interference in the film modulated by electrostriction.

The fundamental and second harmonic spectra displayed in Figure 4 match each other to within the accuracy of the experiment. This similarity would necessarily occur if reflection occurred from the front surface only. However, this is not the case. A measurable signal penetrates through the polymer film and through the semi-transparent gold electrode on the rear surface. The spectral match indicates that the DC field has the same spatial dependence as the applied field which is uniform across the film. This implies that the field responsible for the signal at the fundamental is largely due to charge localized at or near the electrodes. This field may simply be due to the difference between the work functions of the two electrodes, and would be present even if the polymer did not conduct at all, since the Fermi levels of the two electrodes would equilibrate through the external circuit.

Figures 7 and 8 show the fundamental and the second harmonic electroreflection spectra at three different frequencies. At 500 Hz and 1 kHz, the spectra match one another fairly well. At 100 Hz, the magnitude of the reflected signal is significantly larger than at the higher frequencies and the match between the fundamental and second harmonic spectra is somewhat degraded. This difference is tentatively attributed to the detrapping of shallow trapped carriers which will then change the spatial dependence of the applied field.

Figures 9 and 10 show the fundamental and second harmonic electroreflection spectra of a 5 wt% DEH-doped sample before and after it was subjected to a 20V DC field for 15 minutes at room temperature. The changes in the spectrum of the fundamental after the application of the electric field are attributed to charge injection. The amplitude of the fundamental changed drastically, while the amplitude of the second harmonic barely changed. This result supports the assumption that the second harmonic is not dependent on injected charge. Since the amplitude did change, a higher frequency might be needed to insure that the second harmonic signal remains constant. Since the film was more than 70°C below the glass transition temperature, it is assumed that orientation due to the poling field did not occur.

In conclusion, the similarities of the first and second harmonic signals for both the DANS and DEH samples suggest that most of the charge is localized at or near the electrodes. In addition, at lower frequencies (100 Hz) the change in the first harmonic signal of DEH doped sample is attributed to a change in the spatial dependence of the permanent field. The changes in the spectrum of DEH doped polymer film after the application of an electric field are attributed to charge injection. These results are preliminary. More experiments will be performed to confirm these results.

4 - dimethylamino - 4' - nitrostilbene (DANS)
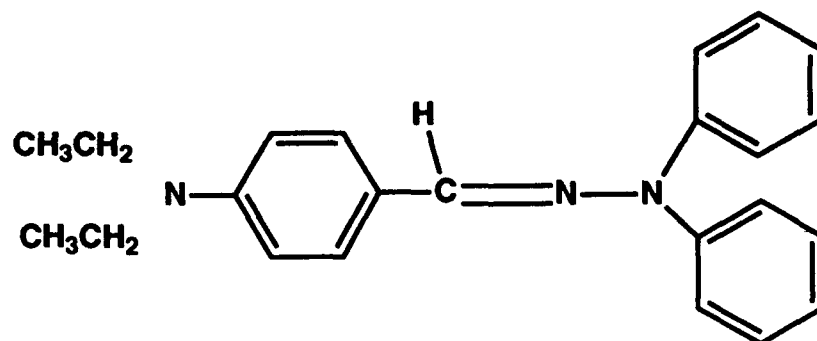
p - diethylaminobenzaldehyde diphenylhydrazone (DEH)

Figure 1. Chromophores used in the experiments.

LP = lamp
L = lens
MC = monochromator
I = iris
P = polarizer
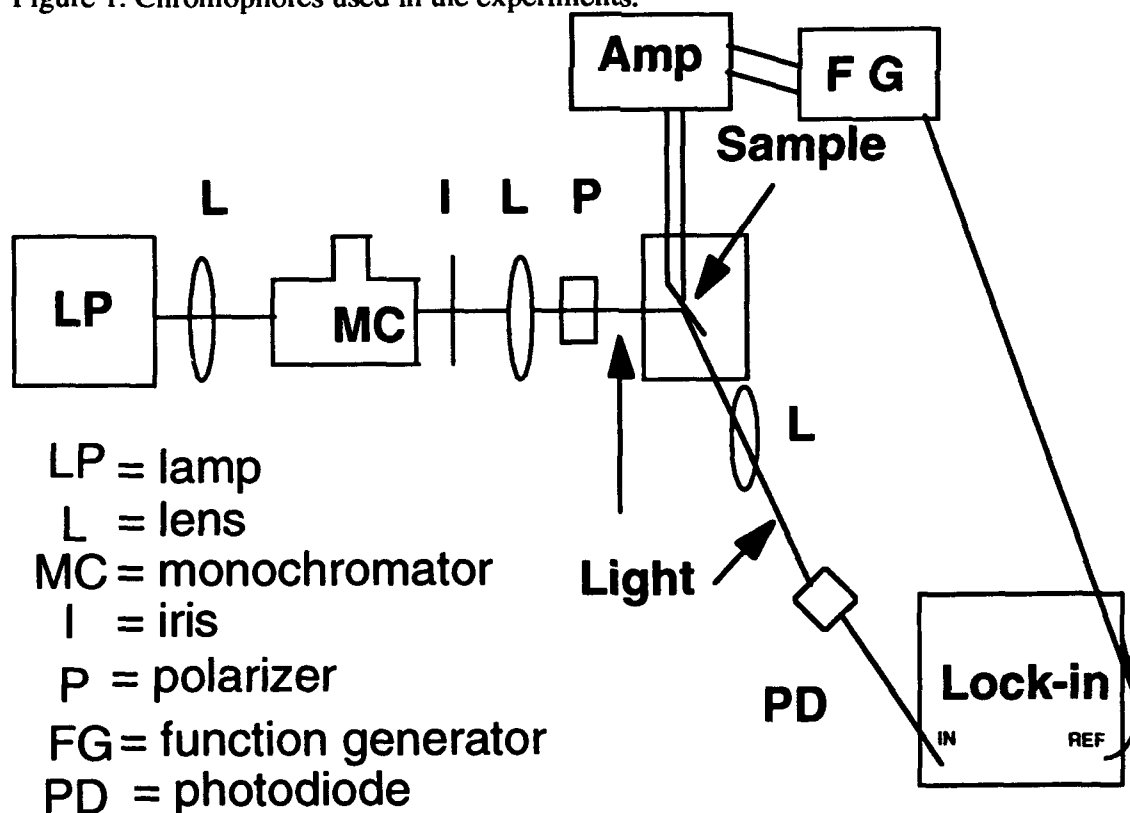FG = function generator
PD = photodiode
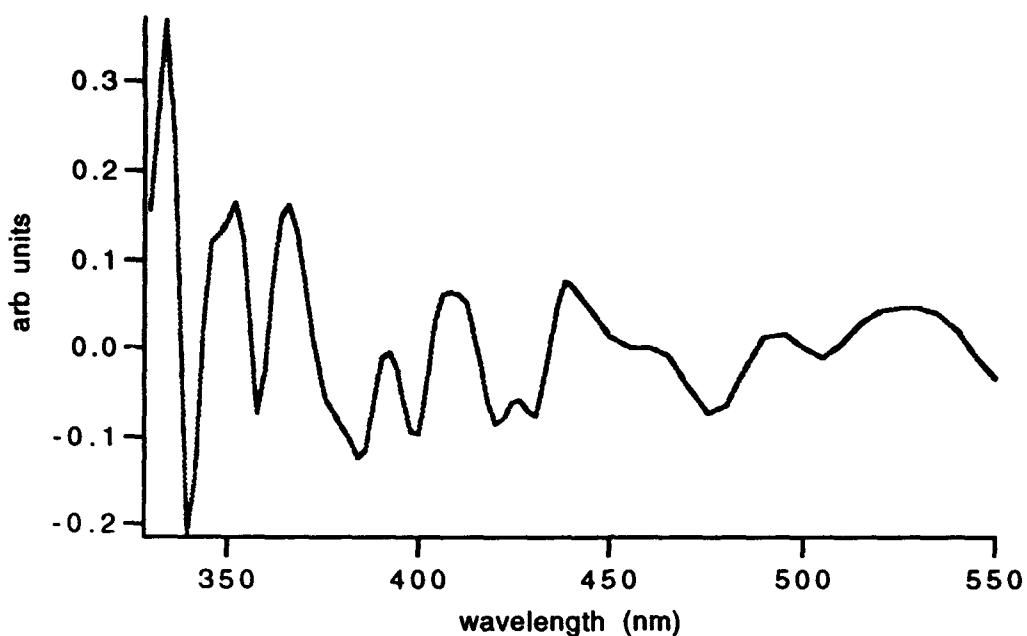
Figure 2. Electroreflection Setup

Figure 3. First derivative of the zero-field spectrum of 5 wt% DANS + PMMA.
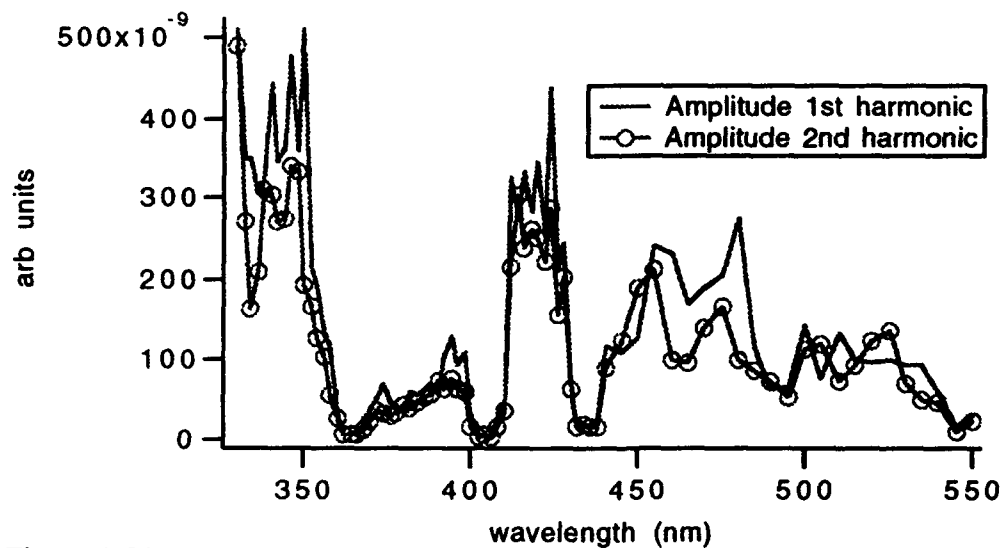

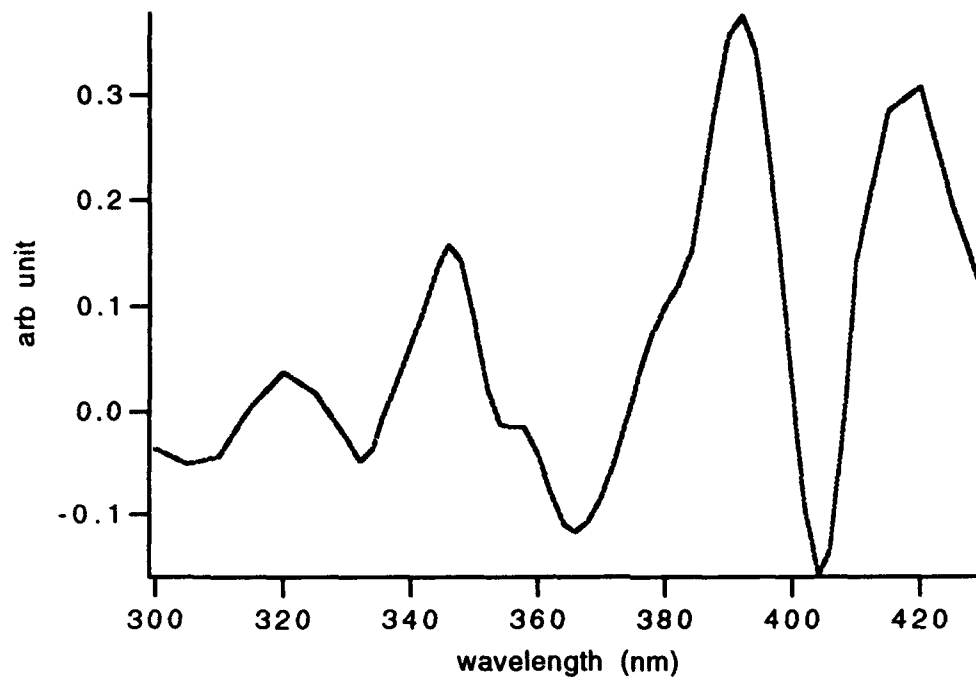Figure 4. First and second harmonic spectra of 5wt% DANS + PMMA.

Figure 5. First derivative of the zero-field spectrum of 5 wt% DEH + PMMA.
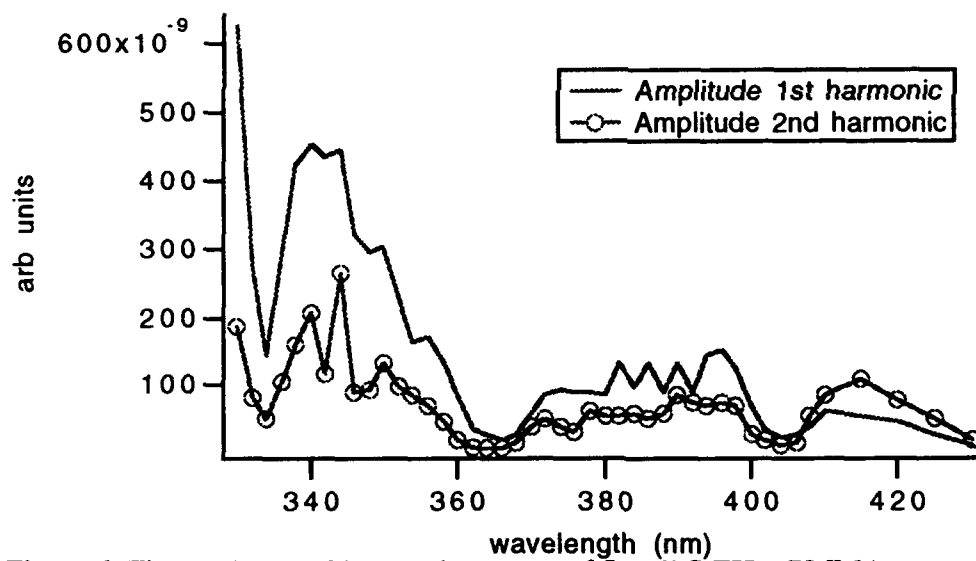

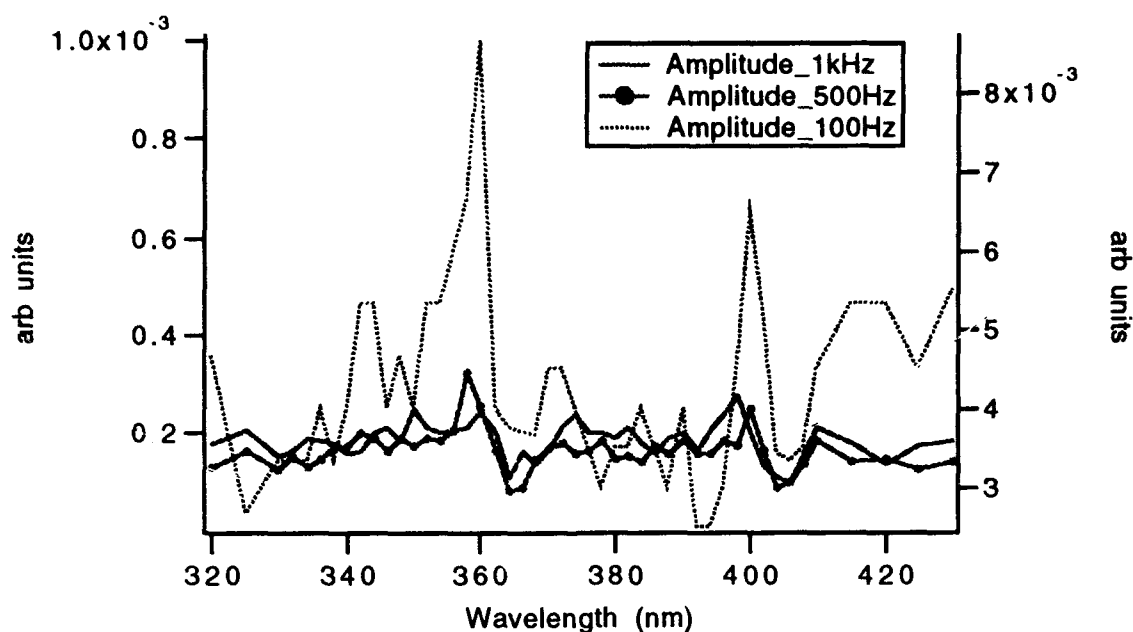Figure 6. First and second harmonic spectra of 5 wt% DEH + PMMA.

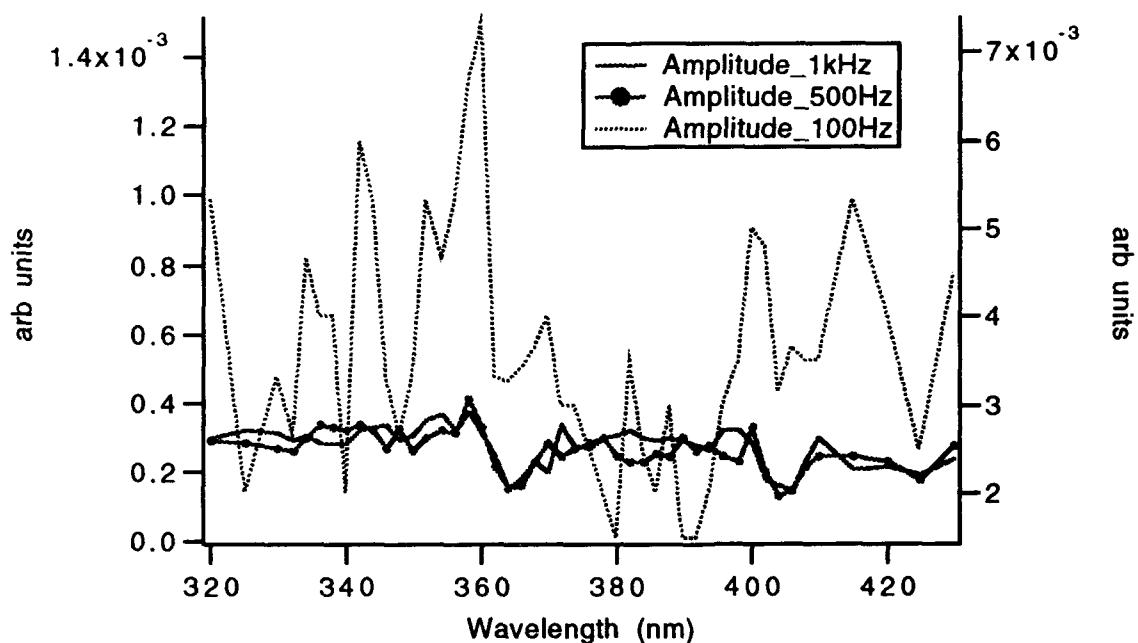Figure 7. First harmonic spectra of 5 wt% DEH + PMMA.

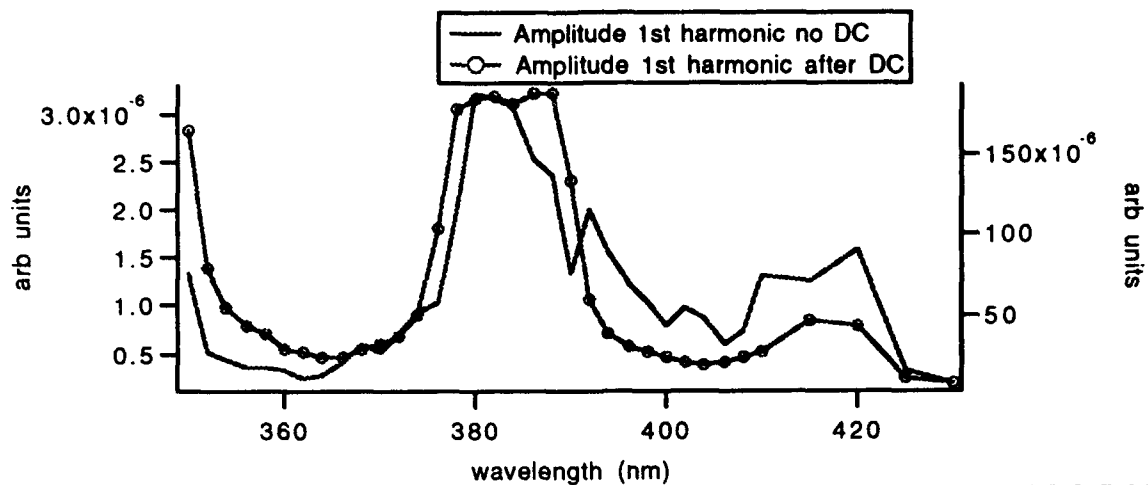Figure 8. Second harmonic spectra of 5 wt% DEH + PMMA.

Figure 9. First harmonic spectra of 5 wt% DEH + PMMA before and after applied DC field .
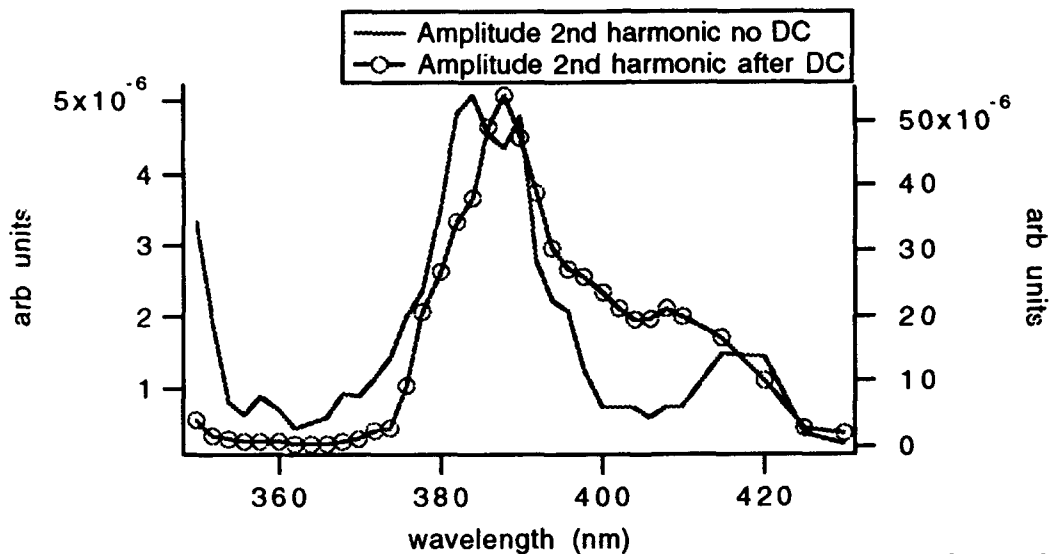
Figure 10. Second harmonic spectra of 5 wt% DEH + PMMA before and after applied DC field.

II.a.2 Second Order Nonlinear Optical Measurements

Key information: *The magnitude of the electric field across the doped thin polymer film and the rotational dynamics of the chromophores in the polymer matrix is obtained.*
Goals answered: *Charge magnitude across the polymer film is obtained as a function of poling and concentration of chromophore. Rotational mobility of the chromophores in the polymer matrix is also obtained as a function of temperature, time, poling, and concentration of chromophore.*

Construction:

A Continuum YAG Surelite I is used to generate 1064 nm laser pulses at 10 Hz. Jobin Yvon monochromator and Hamamatsu photomultiplier tubes are used to collect second harmonic signal. A Tektronix TDS 620 digitizing oscillascope is used as an integrator. The experiment is computer controlled using LabView software and a Macintosh Quadra 950.

Work to date:

The experiment has been recently assembled. Second harmonic generation has been observed using a nonlinear optical chromophore, MNA.

II.a.3 Thermal Pulse Measurements

Key issues: *Charge distribution will be obtained through the polymer film.*
Goals answered: *The charge distribution as a function of film thickness will be obtained for polymer films greater than 10µm.*

In the summer of 1994, Mark Ostrowski, a graduate student, will travel to Gaithersburg, Maryland to conduct thermal pulse experiments at the National Institute of Standards and Technology. These experiments will be conducted with the equipment present at this facility. These studies will be performed in conjunction with Dr. G. T. Davis and Dr. A. DeReggi. These experiments consist of measuring the charge distribution through polymer films doped with second order nonlinear chromophores. The thickness of the films are on the order of 20 µm. Results obtained from these experiments in conjunction with previous-mentioned experiments are used to characterize the electric field effects in poled polymer films.

II.a.4 Total Internal Reflection Fluorescence Spectroscopy

Key issue: *The charge magnitude and distribution across the film will be obtained.*
Goals answered: *The charge distribution through the polymer film as well as the charge magnitude will be obtained as a function of thickness.*

II.b Determine how the applied electric field affects rotational mobility of chromophores in polymer systems.

Methods Used:

The major methods utilized are dielectric relaxation, second order nonlinear optics and Mach Zender Interferometry.

II.b.1 Dielectric Relaxation

Key issues: *The bulk electric field properties such as dielectric constant and dipole moment are obtained. In addition, the rotational dynamics of the chromophore in the polymer matrix as well as the polymer transition temperatures are obtained.*

Goals answered: *The rotational dynamics of the chromophore is obtained as a function of time, temperature, poling and concentration of chromophore.*

Construction:

Temperature dependent dielectric constant is measured using a GenRad 1689 Precision RLC Digibridge. A Delta Design oven, model 9023, is used to regulate the temperature. The entire experiment is computer controlled using LabView software and a Macintos Quadra 950.

II.b.2 Spectroellipsometry:

Key issues: The temperature-dependent index of refraction the dye-doped polymer thin films is investigated as a function of static electric field.

Goals answered: The electrooptic coefficient is determined from the changes in the index of refraction.

Construction:

A Rudolph 1000 Spectroellipsometer is being used to determine the index of refraction spectrum. A temperature-controlled sample housing was constructed by which the temperature could be regulated.

Work to date:

Initial experiments are being performed for calibration of the system and the sample holder. Several models are being tested that will better describe the spun polymer thin film systems.

II.b.3 Interferometry

Key Issues: The second order nonlinearity, the linear electrooptic effect, is determined for thin film doped polymer systems.

Goals answered: Temperature, and temporal dependent electrooptic coefficients are directly measured from the output intensities of a Mach-Zehnder interferometer.

Construction:

A standard and modified (one mirror is replaced with the sample) Mach-Zehnder interferometer is used to determine electric field dependent index of refraction changes in the doped polymer system. A 10 mW HeNe laser is used as the light source. The quasi-static field is generated from a Stanford Research Systems, model DS345, function generator, and is amplified with an University Sound stereo amplifier to the desired values. The applied voltage across the sample is 1 KHz, from 0 to 150 V_{rms}. The experiment is computer controlled using LabView software and a Macintosh Quadra 950. A Stanford Research Systems, model SR530, lock-in amplifier is used to collect data.

APPENDIX A

A1. Electrochromism

Key information: *The magnitude of the electric field at the electrodes and of the average electric field across the polymer film is obtained.*

Goals answered: *Charge symmetry at the surfaces and charge magnitude through the polymer film is obtained as a function of poling and concentration of chromophore.*

Electrochromism is a change in the absorption curve of a chromophore resulting from the application of an external electric field.[6] By applying a DC field across a thin polymer film doped with second order nonlinear optical chromophores, properties of the chromophore can be determined including the dipole moment at the ground state, the change in dipole moment during excitation, and the degree of orientational freedom of the chromophore in a polymer matrix.[7] By applying an AC field across the polymer film, other properties such as the magnitude of the surface field and average electric field through the polymer film can be determined.

The electrochromic effect can be described by a change in the extinction coefficient k, the imaginary part of the complex refractive index (n - ik).[8] The extinction coefficient is related to ε by the relation, $k = 2.303\, Nc\varepsilon/4\pi v$. Therefore the electrochromic effect can be related to the change in the molar extinction coefficient, $\Delta\varepsilon$. Neglecting field dependence of the transition moment, the change in the extinction coefficient with the applied field for a perfectly oriented sample is

$$\frac{\Delta\varepsilon}{Kv} = \frac{1}{h}\left(\underline{p}\cdot\bar{e}\right)^2\left(\Delta\mu\cdot\underline{F}\right)\frac{dS(v)}{dv} - \frac{1}{2h}\left(\underline{p}\cdot\bar{e}\right)^2\left(\Delta\underline{\alpha}:\underline{FF}\right)\frac{dS(v)}{dv}$$
$$+ \frac{1}{2h^2}\left(\underline{p}\cdot\bar{e}\right)^2\left(\Delta\underline{\mu}\cdot\underline{F}\right)^2\frac{d^2 S(v)}{dv^2} \tag{1}$$

where K is a constant, v is the optical frequency, $\underline{p}$ is the field- dependent transition moment, $\bar{e}$ is the polarization vector of absorbed light, $\Delta\mu$ is the change in dipole moment, $\underline{F}$ is the local field, S is the lineshape function of the absorption curve, h is Planck's constant and $\Delta\alpha$ is the change in polarization.[9]

If the absorbing chromophores are isotropically oriented in a rigid polymer matrix and unable to align with the electric field, the linear term in electric field vanishes and one obtains

$$\frac{\Delta\varepsilon}{F^2} = \frac{v}{15h}B\frac{d}{dv}\left[\frac{\varepsilon(v)}{v}\right] + \frac{v}{30h^2}C\frac{d^2}{dv^2}\left[\frac{\varepsilon(v)}{v}\right] \tag{2}$$

where B and C are molecular parameters dependent on the change of polarizability and dipole moment respectively.[10, 11] When the light propagates parallel to the electric field, C can be expressed by the equation

$$C = 3|\Delta\mu|2\,(2 - \cos2\theta) \tag{3}$$

where θ is the angle between $\Delta\mu$ and the direction of the molecular transition moment.[10]

The internal electric field acting on the chromophore is different from the applied electric field. To relate the external applied field to the internal field, the Lorentz equation is used

$$F = \frac{\varepsilon_p + 2}{3}F_o \tag{4}$$

where ε_p is the dielectric constant of the polymer matrix and F_0 is the applied electric field divided by the film thickness.[12] The dielectric constant should be high to increase the internal electric field felt by the chromophore.[13]

Electroreflection is the change in reflectivity of a chromophore due to an applied electric field. The change in reflectance will depend on both the real and imaginary components of the refractive index.[14]

$$\Delta R = \frac{\partial R}{\partial n} \Delta n + \frac{\partial R}{\partial k} \Delta k \qquad (5)$$

Using the relation between k and ε mentioned above, the electrochromic equation can be rewritten as

$$\Delta k = B' \frac{dk}{dv} + C' \frac{d^2 k}{dv^2} \qquad (6)$$

Using the Kramers-Kronig relation to relate Δk to Δn and restricting the range of integration to the relevant absorption bands, it can be shown that

$$\Delta R = B' \frac{dR}{dv} F^2 + C' \left(\frac{\partial R}{\partial n} \frac{\partial^2 n}{\partial v^2} + \frac{\partial R}{\partial k} \frac{\partial^2 k}{\partial v^2} \right) F^2 \qquad (7)$$

where dR/dv is the first derivative of the zero-field reflection spectrum. If an AC field is applied across the doped film, the total field at any point within the film will be the sum of the applied field and any permanent field resulting from differences in the work functions of the electrodes. Since the electric field is squared, this is expressed as

$$F^2 = \left(F_a + F_p \right)^2 = F_a^2 + 2 F_a F_p + F_p^2 \qquad (8)$$

where F_a is the applied field and F_p is the permanent field. The light modulated at the fundamental frequency results from the cross-product of the applied and permanent fields. The light modulated at twice the fundamental frequency results from the applied field only. If the reflection is only off the first surface, the spectrum of the first and second harmonic will be the same. Under this condition, the sign of the permanent field at the interface, $F_p(0)$ is determined from the sign of ΔR_ω and its magnitude is given by

$$F_p \left(0 \right) = \frac{F_a}{4} \frac{\Delta R_\omega}{\Delta R_{2\omega}} \qquad (9)$$

where ΔR_ω and $\Delta R_{2\omega}$ is the change in reflectivity of the first and second harmonic respectively.[14] However, if there is appreciable reflection off the rear surface and the spectrum of the first and second harmonic differ, then the permanent field has a spatial dependence. This spatial dependence implies that charge carriers were injected into the sample. Thus, this will allow us to characterize carrier injection following poling.

Electroabsorption is the change of absorption or transmittance with an applied electric field. To approximate the fractional change in transmittance due to the applied electric field, the space integral over the Beer-Lambert law is used

$$\frac{\Delta T}{T} = -2.303 \int_0^d \Delta\varepsilon \left(x \right) dx \qquad (10)$$

where ΔT is the change in transmittance, d is the thickness of the film, T is the transmittance and $\Delta\varepsilon$ is defined in the electrochromic equation (2).[14] Since an AC field is applied across the

sample, $\Delta T_\omega/T$ is related to the first harmonic signal and $\Delta T_{2\omega}/T$ is related to the second harmonic signal. The potential between the two electrodes is given by

$$V_p = \frac{V_a}{4} \frac{\Delta T_\omega}{\Delta T_{2\omega}}$$ (11)

where V_a is the applied voltage, ΔT_ω and $\Delta T_{2\omega}$ is the change in transmittance of the first and second harmonic signal respectively.[14] This result implies that the ⋁ ⌐unction of one electrode is the value of V_p greater than that of the other electrode.

The changes of reflection (ΔR_ω, $\Delta R_{2\omega}$) and the changes of transm.....ice (ΔT_ω, $\Delta T_{2\omega}$) at the first and second harmonic frequencies can be obtained experimentally. With these values, the surface electric fields and the average electric field across the doped polymer thin film are obtained using equations (9) and (11). The charge symmetry at the surfaces and charge magnitude through the polymer film is then studied as a function of poling and concentration of chromophore. This information provides an insight into the electric field effects on polymer films which is critical for developing efficient poling methods for second order non'·near optical device applications.

A2. Second Order Nonlinear Optical Measurements

Key information: *The magnitude of the electric field across the doped thin polymer film and the rotational dynamics of the chromophores in the polymer matrix is obtained.*
Goals answered: *Charge magnitude across the polymer film is obtained as a function of poling and concentration of chromophore. Rotational mobility of the chromophores in the polymer matrix is also obtained as a function of temperature, time, poling, and concentration of chromophore.*

When a media is subjected to an intense electric field such as a laser beam, the polarization response can be described as

$$P = \chi^{(1)} \cdot E + \chi^{(2)} : EE + \chi^{(3)} \vdots EEE +$$ (12)

where P is the polarization, $\chi^{(1,2,3)}$ are the first, second and third order nonlinear susceptibilities of the medium and E is the optical electric field.[1] Substituting a sinusoidal field equation into this expansion gives[5]

$$P = \chi^{(1)} E_0 \cos(\omega t - kz) + \frac{1}{2}\chi^{(2)} E_0^2 \left[1 + \cos(2\omega t - 2kz) \right]$$
$$+ \chi^{(3)} E_0^3 \left[\frac{3}{4}\cos(\omega t - kz) + \frac{1}{4}\cos(3\omega t - 3kz) \right]$$ (13)

Since second order nonlinear optical processes can only occur in noncentrosymmetric media due to symmetry arguments, second harmonic generation can determine if there is a net orientation of chromophores in the polymer sample.[5] This technique is used to measure the decay of the noncentrosymmetric orientation of the chromophores in doped polymer thin film systems. In addition, $\chi^{(2)}$ in the direction of interest (ZZZ) is directly proportional to the poling field

$$\chi^{(2)}_{zzz} = \frac{\beta N f(\omega)^2 f(2\omega)\mu E}{5 kT}$$ (14)

where β is the microscopic hyperpolarizability, N is the number of chromophores per unit volume, $f(\omega)$ and $f(2\omega)$ are the local field factors for the fundamental and second harmonic

respectively, μ is the dipole moment, E is the electric field, k is Boltzmann's constant and T is temperature.[1] Second harmonic generation measurements can determine the charge magnitude through the film as a function of composition and poling.

If a DC field is applied across the sample, the polarization expression becomes

$$P = \chi^{(1)} E_0 \cos(\omega t - kz) + 2\chi^{(2)} E(0) E_0 \cos(\omega t - kz)$$
$$+3\chi^{(3)} E(0)^2 E_0 \cos(\omega t - kz)+ \ldots \tag{15}$$

where E(0) is the applied field.[1] The term linear with the applied field corresponds to the linear electro-optic effect. Since the polarization is related to the index of refraction, it can be shown that a change in the refractive index due to the linear electro-optic effect can be represented by

$$\Delta\left(\frac{1}{n^2}\right) = rE(0) \tag{16}$$

where n is the refractive index, E(0) is the applied electric field and r is the linear electro-optic coefficient. The linear electro-optic coefficient is related to $\chi^{(2)}$ by the relation[1]

$$r = -\frac{8\pi\chi^{(2)}}{n_0^4} \tag{17}$$

In addition, the electro-optic coefficient can be determined experimentally by the equation

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{\left(n^2 - \sin^2\theta\right)^{\frac{3}{2}}}{\left(n^2 - 2\sin^2\theta\right)} \frac{1}{\sin^2\theta} \tag{18}$$

where λ is the wavelength, I_m is the amplitude of modulation, V_m is the amplitude of the modulating voltage, I_c is the half-intensity point, n is the refractive index, θ is the angle of incidence.[15]

The linear electro-optic coefficient and the decay of $\chi^{(2)}$ is obtained experimentally. With this data, the charge magnitude across the polymer film is obtained as a function of poling and concentration of chromophore. In addition, the rotational dynamics of the chromophores in the polymer matrix is studied as a function of temperature, poling, time and concentration of chromophore. This experiment is unique because it measures the decay rate of the orientation of second order nonlinear optical chromophores in-situ. This information gives insight on the temporal and thermal orientational stability of the chromophores in poled polymer thin film systems.

A3. Dielectric Relaxation

Key issues: *The bulk electric field properties such as dielectric constant and dipole moment are obtained. In addition, the rotational dynamics of the chromophore in the polymer matrix as well as the polymer transition temperatures are obtained.*
Goals answered: *The rotational dynamics of the chromophore is obtained as a function of time, temperature, poling and concentration of chromophore.*

The dielectric constant of a material can be measured with a digibridge over the frequency range 10^{-4} to 10^{10} Hz. In the measurement of the dielectric constant, the polymer is regarded as being electrically equivalent to a capacitor in series or in parallel with a resistor.[16] The real part of the dielectric constant can be expressed as

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direction as approximated in polymer thin films, the two complementary response expressions become

$$\frac{q_A(t)}{A} = \alpha_p a_0 B_0 + (\alpha_p + \alpha_x - \alpha_\epsilon) \sum_{n=1}^{\infty} a_n B_n \exp\left(-\frac{n^2 t}{\tau_1}\right) \qquad (27)$$

after the thermal pulse is applied to the surface x=0 and,

$$\frac{q_K(t)}{A} = \alpha_p a_0 B_0 + (\alpha_p + \alpha_x - \alpha_\epsilon) \sum_{n=1}^{\infty} (-1)^n a_n B_n \exp\left(-\frac{n^2 t}{\tau_1}\right) \qquad (28)$$

where a_0 is proportional to the energy absorbed, B_0 is the mean polarization, a_n and B_n are coefficients of the Fourier cosine series representing the initial temperature distribution and the polarization distribution immediately after the pulse and τ_1 is the thermal relaxation time given by

$$\tau_1 = \frac{d^2}{\pi^2 K} \qquad (29)$$

where K is the thermal diffusivity.[4] The Fourier coefficients can be determined experimentally and can be used to evaluate an approximation for the polarization by the equation

$$P(x) = B_0 + \frac{1}{a_0} \sum_{n=1}^{m} a_n B_n \cos\left(\frac{n\pi x}{d}\right) \qquad (30)$$

In this experiment, the charge distribution as a function of film thickness is obtained for thick polymer film (> 10μm).[4] This result is significant in the study of charge mobility and rotational dynamics of poled chromophores in polymer films. This technique will be used in conjunction with before-mentioned methods to characterize completely the electric field effects on polymer films. Tandem experiments will be performed using electrochromic and thermal pulse methods for films of several millimeters to 10 micron thicknesses; then thinner films can be tested with previously described studies. This allows the development of a "calibration" curve, and will provide useful in analyzing the film thickness dependence of charge independently. The characterization of both thick and thin films is necessary to develop efficient poling techniques for doped polymer films for second order nonlinear optical device applications.

A6. Charge Transport Theories

Charge transport theories modified from literature models will be used to describe the charge distribution as a function of time, temperature, electric field and concentration of dopant. There are two established charge transport theories, the polaron and the gaussian disordered models. These theories model the mobility of charge carriers through polymer films and are briefly described in this section.

The chromophores do not simply sense the applied electric field. As a charge is applied to the surface of a sample, a compensation charge is formed slightly below the surface. This compensation charge will slightly shield the rest of the film from the applied field, thus lowering the effective field. In addition, charge transport through the film and dipole-dipole interactions will effect the local electric field that the chromophore experiences. Therefore, to understand how the electric field affects orientation of the chromophores, it is necessary to understand charge transport through polymer films. There are two models that try to describe this phenomena, the polaron model and the gaussian disordered model.

The polaron theory[20-22] predicts that the charge carrier has strong interactions with some of the molecular vibrations of the dopant molecule on which it resides. These interactions self-trap the charge carrier and form a polaron. A polaron is a combination of a charge carrier and an

elastic deformation.[23] The polaron can only hop from one dopant molecule to another carrying along its molecular distortion. The mobility of the charge carriers is represented by

$$\mu = a_0 \rho^2 \exp\left(-\frac{2\rho}{\rho_0}\right) \exp\left(\frac{-\Delta_0}{kT_{eff}}\right) \exp\left(\frac{\beta E^{0.5}}{kT_{eff}}\right) \tag{31}$$

where a_0, ρ_0 and β are constants, ρ is the distance between dopant molecules, Δ_0 is the zero-field activation energy, k is the Boltzmann's constant, E is the electric field and

$$T_{eff} = \left(\frac{1}{T} - \frac{1}{T_0}\right)^{-1} \tag{32}$$

where T is temperature and T_0 is the reference temperature.

The disorder theory[24-26] predicts that the charge carrier hops from site to site. Each site is a trap requiring a specific activation energy in order to release the charge carrier. The activation energies of the traps are randomized with a Gaussian distribution. The electric field is assumed to shift the energy levels by dropping the energy between hopping sites in a preferred direction. The mobility of charge carriers is represented by

$$\mu = \frac{e}{kT}\left(\frac{a^2 v_0}{6}\right) c^{\frac{2}{3}} \exp\left[-2\gamma a c^{\frac{1}{3}}\right] \exp\left[-\left(\frac{2\sigma}{3kT}\right)^2\right] \exp\left[C\left(-\left(\frac{\sigma}{kT}\right)^2 - \Sigma^2\right) E^{0.5}\right] \tag{33}$$

where e is the charge an electron, a is a lattice parameter, σ and Σ are disorder parameters, γ and C are constants and c is the concentration of dopant.

Both models describe the charge transport through polymer films. It is believed that hopping of both charge carriers and polarons occur. However, experimental data obtained by time of flight measurements are not accurate enough to predict which method of hopping dominates, if any. These experiments can potentially determine the dominant hopping method. In addition, Tom Pasmore, a member of this research group is performing Monte Carlo simulations on charge transport through doped polymer films. These results combined with his simulations will more accurately described charge transport through doped polymer films which is important in optimizing the processing method for second order nonlinear optical device applications.

A7. Polymer Physics

In the study of the rotational dynamics of the chromphores for second order nonlinear applications, both electric field effects and polymer physics are important. At the transition temperatures of a polymer, the polymer physical properties can change dramatically, thus influencing both the rotational dynamics of the chromophore as well as the charge mobility through the polymer itself. Members of this research group are actively studying these polymer physics effects which are briefly described in this section.

Polymers are molecules of extremely high molecular weight. They consist of many repeat units called mers chemically bonded to form a long chain. Due to the chain's length, the polymer does not readily crystallize, but instead forms an amorphous, glassy state. Within this state there are areas of low density called free volume. Because the polymer is not in equilibrium, it slowly relaxes with the passage of time. This relaxation called physical aging, reduces the free volume and changes the mechanical, electrical and optical properties of the polymer.[27] Physical aging and local mobility are dependent on the composition and molecular weight of the polymer as well as the temperature. An increase in temperature will increase the mobility of polymer segments within the chain and will therefore increase the relaxation rate of a polymer.

A polymer has many aburpt changes in its physical properties at relatively discrete temperatures called transition temperatures. The first transition temperature (T_g or T_α) is related to large scale polymer backbone motion and occurs when the polymer goes from a liquid-like to a glass-like state.[28] Another transition temperature, T_β, is related to the motion of side groups.[16] Below this temperature, the motions of side groups are halted.

The rotational dynamics of the chromophore is dependent strongly on its local environment. Local mobility of the polymer determines the rotational dynamics of the chromophore and its relaxation rate. This relaxation can be modeled with the empirical Williams-Watt equation

$$R(z) = \exp\left(\frac{-z}{\tau_r}\right)^\beta$$

(34)

where τ_r is the characteristic retardation time and β is the width of the spectrum of retardation.[27]

Polymer physics affects the rotational dynamics of poled chromophores in polymer thin films. This information gives insight on the temporal and thermal orientational stability of the chromophores for second order nonlinear optical applications.

The effect of large magnitude electric fields on polymer thin films is investigated in order to improve poling efficiencies in polymer films for second order nonlinear optical applications. This research determines the charge distribution, symmetry, and magnitude across doped and undoped glassy polymer thin films as a function of temperature, time, and poling (processing). Electrochromism, second order nonlinear optics, dielectric relaxation, isothermal current and surface voltage decay measurements will be used to determine the material properties. Trapping levels and sites will also be examined. By using dielectric relaxation and optical techniques we will explore how applied electric fields affect rotational mobility of small chromophores in polymer hosts. We expect to be able to improve poling efficiency and thus device performance both by achieving the greatest possible fields with the best magnitude and symmetry characteristics, and enhancing the temporal and thermal properties of the films by manipulating their charge storage and transport properties. This understanding will allow the most efficient development and design for nonlinear optical materials.